# CHEMICAL REPORT

ON THE

# MODE OF DETECTING VEGETABLE SUBSTANCES MIXED WITH COFFEE

FOR THE PURPOSE OF ADULTERATION.

BY

PROFESSOR GRAHAM, DR. STENHOUSE, AND MR. DUGALD CAMPBELL.

ADDRESSED TO THE CHAIRMAN OF THE BOARD OF INLAND REVENUE,

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The adulteration of coffee in the condition of the original bean, unground and unroasted, could only be effected by the substitution of a different seed, and would form the subject of an inquiry entirely botanical. But it is proper to remark that the coffee-bean is liable to be rendered entirely worthless, without any injury to its structure, when kept in a wet or damp state for some time,—apparently from the readiness with which the soluble constituents of the bean spontaneously ferment. Coffee damaged by sea-water has been found to retain neither the aroma nor bitter flavour of the seed, and to have lost the whole of its characteristic principle, caffeine. The entire soluble matter which can be extracted from the damaged seeds by boiling water is greatly reduced, and does not exceed 12 per cent. of their weight, while the presence of the salts of sea-water is always sufficiently obvious.

The coffee-bean, in its fresh, unprepared state, is tough, and ground with difficulty. It yields an infusion without aroma, which is bitter, and is said to act more powerfully on the nerves than roasted coffee. This seed, however, is always roasted before being made use of, and it is in that state, and with its structure more or less obliterated by grinding, that it must be identified, and its purity established by chemical means of investigation.

In consequence of torrefaction, coffee is materially altered, and acquires new properties. The woody tissue of the fresh bean is

horny, and differs from ordinary woody fibre in its composition, and is also said not to yield sugar when treated with sulphuric acid. By the roasting, this woody tissue undergoes a partial decomposition, and becomes friable, and the difficulty of pulverising the seed, and exhausting it by water, is removed. There is produced at the same time a soluble brown bitter matter, due in part to a gummy substance pre-existing in the coffee, altered like starch by torrefaction, but principally to the conversion into caramel of a quantity of sugar in the coffee-bean, amounting to 6 or 7 per cent. of its weight.

A still more characteristic product of the roasting of coffee, is that which gives it aroma. This principle, when separated from the infusion of coffee by distillation, is found to be a brown liquid oil, heavier than water, soluble in ether, and has received the name of *Caffeone* (Boutron and Frémy). Caffeone is slightly soluble in boiling water; a quantity of caffeone which is almost insensible will aromatise two or three pints of water.

In common with all the valuable constituents of coffee, caffeone is found to come from the soluble portion of the roasted seed.

The caffeic acid of the green coffee is also changed by the roasting into an acid of different properties.

Of the crystallisable caffeine, a small portion may be lost from its volatility in roasting.

No seed appears to be known, which, roasted and pulverised, forms a true equivalent and sufficient substitute for coffee, either in the physiological properties or chemical composition of its soluble extract. A great variety of seeds were tried in France, as substitutes for coffee, during the continuance of the Continental blockade, including, in addition to maize, barley, oats, and the other cereals, the seeds of the yellow flag (*Iris pseudo-acorus*), grey pea (*Cicer arietinum*), the milk vetch, or Andalusian astragalus (*Astragalus boeticus*), the *Hibiscus esculentus*, holly, Spanish broom, acorns, chesnuts, the small lupin (*Lupinus angustifolia*), peas, haricots, horse-beans, sunflower, pips of the gooseberry and grape, eglantine (*Rosa villosa*), and the capsules of box (*Buxus sempervirens*). Of the seeds enumerated, the yellow flag, a common marsh plant in England, appears to have offered the only similarity to coffee; but it is doubtful whether the resemblance extended beyond the aroma of this seed when roasted, which is certainly suggestive of coffee.

The search made among the seeds of other plants for a substitute for the coffee-berry may then be said to have entirely failed.

The divergence of the root-substitutes from true coffee is still greater in every property except one. The roots which have been most used are those of chicory (*Cichorium intybus*), carrot,

beet, rush-nut (*Cyperus esculentus*), earth-nut (*Arachis hypogæa*), scratch-weed (*Gallium aparine*), fern (*Polypodium filix mas*), and butchers' broom (*Ruscus aculeatus*).

The roots of chicory, and of beet and carrot, which are all extensively used in Germany, are similarly prepared, being cut into thin slices, dried in a stove, and then passed through a coffee-roaster,—generally with the addition of about 2 per cent. of butter, and sometimes of a red powder, to give the colour of coffee.

It is to be remarked of the roots, that they are generally used rather as an addition to coffee than as a substitute for it. In one property these roots all agree, and we have no doubt that it has led to this common application of them : chicory, beet, carrot, &c., are all remarkable for containing a large quantity of sugar, easily caramelised by heat. They acquire, when roasted, the bitter of burnt sugar, with a somewhat similar aroma. Now the taste of this bitter appears to be one of the strongest and most general of our gustatory preferences. It equally recommends toast-water, and the varieties of brown beer or porter, in the preparation of which a portion of malt is used with its sugar caramelised by heat. The caramel bitter is, in fact, a stock flavour, which we find modified by the most various accessories in different beverages, and even in solid articles of diet in a cooked state. It is not surprising, therefore, that the chicory root, containing as it does about 30 per cent. of sugar, more than one-half of which is caramelised in roasting, should obtain extensive favour as an addition to coffee. Fresh chicory has a certain bitterness, or rather acridity, but this is overpowered in the torrefied root by the caramel bitter, and this root may be adequately replaced by the bland beet or carrot similarly prepared. No one of these roots contains any constituent which associates it with coffee, except sugar :—in other respects they are entirely different.

The preparation of roasted chicory appears to have originated in Holland upwards of a century ago, but remained secret till 1801. It is now prepared on a great scale, both on the Continent and in England. The quantity of chicory-powder consumed annually in France is known to amount 6,000,000 kilogrammes.

In the chemical examination of ground coffee, with the view to discover if it is mixed with the vegetable substances which have been named, or with others, the characteristic constituents of the coffee are less immediately available than certain properties of the infusion of a physical character. This arises from the circumstance, that although it is easy to discover the presence of caffeic acid and caffeine, yet the determination of the exact quantity of these substances in an infusion is both difficult and tedious.

There is reason also to believe that the proportion of caffeic acid

and caffeine varies considerably in different samples of coffee, so that the quantities of these substances (when found) could not show exactly the proportion of pure coffee in a mixture. It will be most advantageous to discuss here the general properties of the coffee infusion, in the first instance, as they are most easily observed; and a single character of this kind in some instances, and two or three in others, will generally be sufficient to establish adulteration when it has been practised. The higher chemical inquiries will then follow.

1. When hot water is applied to the powder of chicory and other roots, it softens immediately, from the facility with which water is imbibed, while the grains of coffee remain hard and gritty in the same circumstances. Ground chicory is highly hygroscopic.

Roasted grain, such as wheat and barley, gives an infusion with hot water, which is mucilaginous and thick, while the infusion of coffee is remarkably thin and limpid. The grain infusion generally contains starch, and gives, when cool, a blue colouration with iodine, while the infusions of both coffee and chicory appear to be entirely destitute of starch.

2. The more deep and rapid coloration of water by chicory and the allied roots than by coffee, affords a useful indication in a preliminary examination. The roasted grains also appear to colour water more deeply than coffee does. The relative colouring power of coffee, chicory, and a variety of other vegetable substances used in the adulteration of coffee, was determined with considerable precision by infusing equal quantities of each in water, as in the preparation of coffee, filtering the infusions through paper, and observing the colour in glass tubes of equal diameter—about 1 inch. The solutions required to be very dilute. It was also necessary to have a standard of comparison, and for this purpose caramel, carefully prepared from cane-sugar, was had recourse to. The standard solution of caramel consisted of 1 grain of that substance dissolved in 2000 grains of water. To produce the same intensity of colour as the standard solution, a larger proportion than 1 grain of all the other substances required to be dissolved in 2000 grains of water. The proportion necessary is expressed in Table I. The substances are all roasted, as they would be used to mix with coffee.

### Table I.

Weight of substanee (roasted) dissolved in 2000 parts of water, to produce an equal depth of colour.

| | |
|---|---|
| Caramel | 1· |
| Mangold-wurzel | 1·66 |
| Bouka (a coffee substitute) | 1·66 |
| Sparke's vinegar eolouring | 1·74 |
| Blaek malt | 1·82 |
| White turnips | 2·0 |
| Carrots | 2·0 |
| Chicory (darkest Yorkshire) | 2·22 |
| Parsnips | 2·5 |
| Maize | 2·86 |
| Rye | 2·86 |
| Dandelion root | 3·33 |
| Red beet | 3·33 |
| Bread raspings | 3·64 |
| Acorns | 5·00 |
| Over-roasted eoffee | 5·46 |
| Highly-roasted coffee | 5·77 |
| Medium-roasted coffee | 6·95 |
| Another speeimen of coffee | 6·66 |
| White lupin seed | 10·00 |
| Peas | 13·33 |
| Beans | 13·33 |
| Spent tan | 33· |
| Brown malt | 40· |

It will be seen from the preceding table, that 2·22 parts of ehieory have the same eolouring power as 5·77 grains of highly-roasted, and 6·95 grains of medium-roasted eoffee, or of 13·33 grains of roasted peas, and 40 parts of brown malt.

The same results are given in a different form in Table II.

### Table II.

Colouring power of various substanees (roasted) dissolved in an equal quantity of water.

| | |
|---|---|
| Caramel | 1000· |
| Mangold-wurzel | 602·4 |
| Bouka (a eoffee substitute) | 602·4 |
| Sparke's vinegar eolouring | 574·71 |
| Blaek malt | 549·45 |
| White turnips | 500· |
| Carrots | 500· |
| Chicory (darkest Yorkshire) | 450·45 |

| | |
|---|---|
| Parsnips | 400· |
| Maize | 350· |
| Rye | 350· |
| Dandelion root | 300·3 |
| Red beet | 300·3 |
| Bread raspings | 274·72 |
| Acorns | 200· |
| Over-roasted coffee | 183·15 |
| Highly-roasted coffee | 173·31 |
| Medium-roasted coffee | 143·88 |
| Another specimen of coffee | 150·15 |
| White lupin seed | 100· |
| Peas | 73·18 |
| Beans | 75·18 |
| Spent tan | 30· |
| Brown malt | 25· |

The number for chicory (450) indicates that that substance possesses nearly half the colouring power of caramel (1000); while highly-roasted coffee (173) is about one-sixth of caramel. Maize and rye, with probably all the other cereals, rise to 350, and have therefore a high colouring power, quite double that of coffee; while peas and beans (75) are on the other side, and possess only about half the colouring power of coffee for equal weights of the substances compared.

The preceding solutions were prepared at 212°, and chicory then exhibits about three times the colouring power of coffee. But when the solutions are prepared without heat, the disparity is still greater. In cold water chicory exceeded coffee about four and a half times in colouring power.

When a few grains of roasted chicory, or any other sweet root, are dropped into a glass of cold water, without being stirred, a yellowish-brown colour diffuses rapidly through the liquid, while the pure coffee gives no sensible colour to the water in similar circumstances.

3. Another property of infusions, which is still more precise and valuable, is their specific gravity.

The proportion of substance found most suitable for an extensive comparison was 1 in 10 of water. The substances were not exhausted by water, but simply placed in about a pint of cold water, in the preceding proportion by weight, and the temperature raised to 212°, and retained at that point for not more than half a minute. The infusions were then filtered through paper. The substances, as usual, are roasted and ground equally fine, with the exception of the last three in the table.

TABLE III.

Specific gravity of solutions at 60° F., 1 part of substance to 10 parts of water.

| | |
|---|---|
| Spent tan | 1002·14 |
| Lupin seed | 1005·7 |
| Acorns | 1007·3 |
| Peas | 1007·3 |
| Mocha coffee | 1008·0 |
| Beans | 1008·4 |
| Neilgherry coffee | 1008·4 |
| Plantation Ceylon coffee | 1008·7 |
| Java coffee | 1008·7 |
| Jamaica coffee | 1008·7 |
| Costa Rica coffec | 1008·98 |
| Nativc Ceylon coffee | 1009·0 |
| Costa Rica coffee | 1009·5 |
| Brown malt | 1010·9 |
| Parsnips | 1014·3 |
| Carrots | 1017·1 |
| Bouka | 1018·5 |
| English chicory (Yorkshire) | 1019·1 |
| Black malt | 1021·2 |
| Turnips | 1021·4 |
| Rye meal | 1021·6 |
| English chicory | 1021·7 |
| Dandclion root | 1021·9 |
| Red bect | 1022·1 |
| Foreign chicory | 1022·6 |
| Guernsey chicory | 1023·2 |
| Mangold-wurzel | 1023·5 |
| Maize | 1025·3 |
| Bread raspings | 1026·3 |
| British gum | 1037·9 |
| Gum arabic | 1038·6 |
| Cane sugar | 1040·9 |
| Starch sugar | 1042·8 |

The leguminous seeds, it appears, givc a low specific gravity,—peas 1007·3, and beans 1008·4. The coffees are also remarkably low, varying from Mocha coffee 1008·0, to Costa Rica 1009·5; while chicory riscs greatly, ranging in different samples between 1019·1 and 1023·2. The cereals are equally high, or still higher, in the scale of gravity; rye-meal being 1021·6, and maize 1025·3. The low gravity of the coffee infusion, therefore, distinguishes it sharply from the two most important classes of adulterating substances,—the roots and cereals.

4. The action of other solvents, besides water, may be shortly referred to.

Agitated four times successively in ten times their weight of ether, the substances to be mentioned gave different proportions of matter soluble in that menstruum:—

| | | | | | |
|---|---|---|---|---|---|
| Roasted | beans . . . | 1·81 | per cent. of oil | and | resin, |
| ,, | maize . . . | 5·15 | ,, | ,, | ,, |
| ,, | chicory (Yorkshire) | 6·83 | ,, | ,, | ,, |
| ,, | coffee (Mocha) . | 15·93 | ,, | ,, | ,, |

including probably nearly 1 per cent. of caffeine.

It thus appears that coffee yields much more soluble matter to ether than beans, maize, or chicory, which represent the three classes of leguminous seeds, cereals, and sweet roots. The fat obtained from chicory was no doubt principally composed of the sweet American or Australian tallow, added by English manufacturers to the root, in roasting, to prevent burning. The experiment with ether is easily made, and may in particular circumstances prove valuable.

The solubility of the same substances in proof spirit was observed, the substance being exhausted four times in succession by ten times its weight of proof spirit, at the boiling temperature.

Roasted beans gave 17·5 per cent. of a dry, blackish, lustrous extract.

Roasted maize gave 50·2 per cent. of an extract much like the preceding.

Roasted chicory (Yorkshire) gave 67·76 per cent. of extract of a lighter colour than the preceding, but otherwise very similar.

Roasted coffee (Mocha) gave 26·35 per cent. of extract, much like the first two in external appearance.

These operations are remarkably tedious, while the experiments with ether, on the contrary, are easy and simple. The results with proof spirit are not sufficiently characteristic to recommend its application.

5. Fermentation by means of yeast gives a decisive proof of the adulteration of coffee by many vegetable substances, particularly by chicory and the other saccharine roots.

In our fermentation experiments, 2000 grains of the coffee or other substances were weighed out, and treated successively with $1\frac{1}{2}$ pint of cold water, $1\frac{1}{2}$ pint of water about 174°, and a little additional water for washing the solid residue upon a filter of fine calico. About 3 pints of infusion were thus obtained, which were mixed with 250 grains of brewers' yeast, weighed after being pressed in a calico bag. The fermentation was continued for forty-eight hours at a temperature of from 80° to 90°. The fermented liquor was afterwards distilled, and about 6000 grains

brought over. The last vinous liquor was rectified a second time, about 3000 grains being now collected; and the alcohol was inferred from the density of this distillate.

The substances were examined for sugar both before and after being roasted, as it was interesting to observe the extent to which the sugar is caramelised, by torrefaction, in the different substances.

The sugar of coffee is found to be reduced by roasting from 6 to 7 per cent. in raw coffee, to from 0· to 1·12 per cent. in the roasted,—or to be almost entirely destroyed; while in other substances the sugar is more generally reduced, by precisely similar treatment, to from one-half to one-third of its original proportion. It is difficult to account for this dissimilarity, unless a portion of the sugar of raw coffee exists in a state of conjugate combination, like the sugar in tannin, amygdalin, salicin, &c.: our attempts to isolate such a conjugate body, however, from raw coffee, have not yet proved successful, and its existence is therefore hypothetical. We succeeded, on the other hand, in crystallising out cane-sugar from an infusion of raw coffee. It was decided by proper experiments that the fermentation of sugar was not interfered with by the empyreumatic products, or essential oil of roasted coffee.

The sugar was determined which exists in the most dissimilar varieties of coffee, the wild and cultivated beans, the beans from Ceylon and the West Indies, from Arabia, and the Neilgherry Hills. Twelve different samples were examined, each both before and after roasting.

TABLE IV.

Sugar found in coffee, before and after torrefaction.

| | Sugar per Cent. | |
|---|---|---|
| | Raw. | Roasted. |
| 1. Plantation Ceylon . . | 7·52 | 1·14 |
| 2. " " . . | 7·48 | 0·63 |
| 3. " " . . | 7·70 | 0·0 |
| 4. " " . . | 7·10 | 0·0 |
| 5. Native Ceylon . . . | 5·70 | 0·46 |
| 6. Java . . . . . | 6·73 | 0·48 |
| 7. Costa Rica . . . . | 6·72 | 0·49 |
| 8. " " . . . . | 6·87 | 0·40 |
| 9. Jamaica . . . . | 7·78 | 0·0 |
| 10. Mocha . . . . | 7·40 | 0·50 |
| 11. " . . . . | 6·40 | 0·0 |
| 12. Neilgherry . . . . | 6·20 | 0·0 |

The sugar in coffee appears to be increased by cultivation,—the proportion in Native Ceylon being 5·7 per cent., and in Plantation Ceylon from 7·1 to 7·7 per cent.

The proportion of sugar in the dried roots is high at first, and continues after roasting still very notable.

TABLE V.

Sugar in chicory and other sweet roots, before and after torrefaction.

| | Sugar per Cent. Raw. | Roasted. |
|---|---|---|
| Foreign chicory . . . | 23·76 | 11·98 |
| Guernsey chicory . . . | 30·49 | 15·96 |
| English chicory . . . | 35·23 | 17·98 |
| ,, ,, (Yorkshire) . | 32·06 | 9·86 |
| Mangold-wurzel . . . | 23·68 | 9·96 |
| Carrots (ordinary) . . | 31·98 | 11·53 |
| Turnips ,, . . . | 30·48 | 9·65 |
| Beet root (red) . . . | 24·06 | 17·24 |
| Dandelion root . . . | 21·96 | 9·08 |
| Parsnips . . . . | 21·70 | 6·98 |
| Bouka (a coffee substitute) . | — | 5·82 |

It thus appears that roasted chicory, as it is sold for mixing with coffee, retains from 9·86 to 17·98 per cent. of undecomposed sugar. In none of the other sweet roots which are occasionally substituted for chicory, such as mangold-wurzel, beet, turnip, or carrot, does the proportion of sugar retained after torrefaction fall under 9 per cent., with the exception of parsnip, in which the sugar falls to 6·98 per cent. The coffee substitute, "Bouka," falls into this class, and appears to be a mixture of true coffee with a torrefied sweet root.

The last group is composed of the leguminous and certain other seeds, with the cereals. The sugar was determined for most of these substances in the roasted form of the grain only, which alone affects the question of adulteration.

TABLE VI.

Sugar in various seeds, before and after torrefaction.

| | Sugar per Cent. Raw. | Roasted. |
|---|---|---|
| Acorns . . . | 3·64 | 2·70 |
| Horse-beans . . | — | 1·62 |
| Peas (grey) . . | — | 1·08 |
| Maize . . . | — | 0·82 |
| Rye-meal . . . | — | 1·96 |
| Bread-raspings . . | — | 1·78 |
| Lupin-seed . . | — | 0·74 |
| Brown malt . . | 8.48 | — |
| Black malt . . . | — | 1·66 |

In the roasted seeds enumerated, the proportion of sugar is sensible, but not sufficiently considerable to give the means of distinguishing leguminous seeds and cereals from coffee. In roasted acorns, the sugar rises to 2·7 per cent., and black malt, it will be observed, still retains 1·66 per cent. of fermentable matter.

The fermentation test, on the other hand, is adapted to detect adulteration by chicory and the sweet roots, and will, we believe, from its certainty and facility of application, prove eminently useful for that purpose.

6. Coffee, and the various vegetable substances used in its adulteration, may be incinerated on a platinum or porcelain capsule, and leave an earthy ash, of which the composition is often characteristic of the plant. Valuable information may be obtained, without making a formal analysis of the ash, by simply digesting it in strong hydrochloric acid. The earth which remains undissolved after this treatment is silica. Now coffee, we find, is remarkably distinguished from the roots and cereals, by the small quantity of silica it affords. The quantity of that earth found in coffee is so small, that it may be doubted whether coffee contains any silica except what may accidentally adhere to the coffee beans, when collected, in the form of sand. The proportion of silica found in the twelve samples of coffee of Table IV. was as follows:—

TABLE VII.

Silica in roasted coffee.

| | Per Cent. in Ash. |
|---|---|
| Sample 1 | 0· |
| „ 2 | 0· |
| „ 3 | 0·26 |
| „ 4 | 0·02 |
| „ 5 | 0·17 |
| „ 6 | 0·28 |
| „ 7 | 0· |
| „ 8 | 0·45 |
| „ 9 | 0· |
| „ 10 | 0· |
| „ 11 | 0· |
| „ 12 | 0·09 |

The only case in which the silica approaches to half a per cent. of the ash is Sample 8; and in another sample of the same coffee, which was properly screened before roasting, the silica of the ash fell to 0.

On the other hand, the silica and sand, insoluble in acids, of four samples of roasted chicory, amounted to so much as 10·69,

13·13, 30·71, and 35·85 per cent. of the ash. It may be added, that the portion of this silica soluble in alkali was, in the same samples, 2·61, 3·81, 10·52, and 12·75 parts; the portion of silica insoluble in alkali, 8·08, 9·32, 20·19, and 23·10 parts.

The whole silica in roasted dandelion root amounted to 11·26 per cent. of the ash.

In other cultivated roots the proportion of silica does not appear to be so large as in chicory. The silica is always expressed with reference to 100 parts of the ash. Messrs. Way and Ogston find in the root of the carrot from 0·76 to 1·92 silica; in beet, from 1·4 to 4·11 silica; and in turnip, from 0·96 to 2·75 silica.

The proportion of silica appears to be low in certain grains and seeds, although rarely descending to the insignificant proportion of the coffee-bean,—and to be very high in other grains. We find in the ashes of acorns 1·01 per cent. of silica; in maize, 1·78 per cent. of silica; in the white lupin of the Levant, 0·87 per cent. of silica. Messrs. Ogston and Way report from 2·05 to 5·46 silica for wheat; from 23·6 to 70·77 silica for barley; from 38·48 to 50·03 for oats; and 9·22 for rye.

It appears, therefore, that the presence of 1 per cent. or upwards of silica in the ashes of coffee is a proof of adulteration; that the adulterating substances which increase the proportion of silica most considerably are oats and barley, then chicory and dandelion, which are followed by rye: wheat, beet, turnip, and carrot, would produce a small and less decisive effect.

There will now be presented complete analyses, made for this inquiry, of the ashes of seven varieties of coffee, and four different samples of chicory.

TABLE VIII.

Analyses of the ashes of coffee and chicory.

COFFEE.

| | Plantation Ceylon | Native Ceylon | Java. | Costa Rica. | Jamaica. | Mocha. | Neilgherry. |
|---|---|---|---|---|---|---|---|
| Potash | 55·10 | 52·72 | 54·00 | 53·20 | 53·72 | 51·52 | 55·80 |
| Soda | — | — | — | — | — | — | — |
| Lime | 4·10 | 4·58 | 4·11 | 4·61 | 6·16 | 5·87 | 5·68 |
| Magnesia | 8·42 | 8·46 | 8·20 | 8·66 | 8·37 | 8·87 | 8·49 |
| Sesquioxide of iron | 0·45 | 0·98 | 0·73 | 0·63 | 0·44 | 0·44 | 0·61 |
| Sulphuric acid | 3·62 | 4·48 | 3·49 | 3·82 | 3·10 | 5·26 | 3·09 |
| Chlorine | 1·11 | 0·45 | 0·26 | 1·00 | 0·72 | 0·59 | 0·60 |
| Carbonic acid | 17·47 | 16·93 | 18·13 | 16·34 | 16·54 | 16·98 | 14·92 |
| Phosphoric acid | 10·36 | 11·60 | 11·05 | 10·80 | 11·13 | 10·15 | 10·85 |
| Silica | — | — | — | — | — | — | — |
| Sand | — | — | — | — | — | — | — |
| Total amount | 100·63 | 100·20 | 99·97 | 99·06 | 100·18 | 99·68 | 100·04 |

## CHICORY.

DEDUCTING SAND AND SILICA.

| | Darkest English (Yorkshire) | English. | Foreign. | Guernsey. |
|---|---|---|---|---|
| Potash | 38·53 | 27·85 | 46·07 | 46·27 |
| Soda | 9·34 | 16·90 | 3·17 | 5·49 |
| Lime | 10·79 | 10·81 | 7·78 | 7·65 |
| Magnesia | 6·06 | 8·08 | 5·33 | 5·55 |
| Sesquioxide of iron | 4·38 | 3·50 | 8·29 | 5·08 |
| Sulphuric acid | 11·38 | 11·78 | 8·38 | 8·67 |
| Chlorine | 5·67 | 5·23 | 5·03 | 6·58 |
| Carbonic acid | 2·04 | 3·22 | 4·36 | 4·60 |
| Phosphoric acid | 12·27 | 12·61 | 11·00 | 9·59 |
| Silica | — | — | — | — |
| Sand | — | — | — | — |
| Total amount | 100·46 | 99·98 | 99·41 | 99·48 |

DEDUCTING SAND AND NOT SILICA.

| | Darkest English (Yorkshire) | English. | Foreign. | Guernsey. |
|---|---|---|---|---|
| Potash | 37·07 | 27·13 | 40·20 | 41·41 |
| Soda | 8·99 | 16·46 | 2·77 | 4·92 |
| Lime | 10·38 | 10·53 | 6·79 | 6·85 |
| Magnesia | 5·83 | 7·87 | 4·66 | 4·97 |
| Sesquioxide of iron | 4·22 | 3·41 | 7·24 | 4·55 |
| Sulphuric acid | 10·95 | 11·48 | 7·32 | 7·76 |
| Chlorine | 5·46 | 5·10 | 4·39 | 5·89 |
| Carbonic acid | 1·97 | 3·14 | 3·81 | 4·12 |
| Phosphoric acid | 11·81 | 12·29 | 9·60 | 8·59 |
| Silica | 3·81 | 2·61 | 12·75 | 10·52 |
| Sand | — | — | — | — |
| Total amount | 100·49 | 100·02 | 99·53 | 99·58 |

NOT DEDUCTING SAND AND SILICA.

| | Darkest English (Yorkshire) | English. | Foreign. | Guernsey. |
|---|---|---|---|---|
| Potash | 33·48 | 24·88 | 29·56 | 32·07 |
| Soda | 8·12 | 15·10 | 2·04 | 3·81 |
| Lime | 9·38 | 9·60 | 5·00 | 5·31 |
| Magnesia | 5·27 | 7·22 | 3·42 | 3·85 |
| Sesquioxide of iron | 3·81 | 3·13 | 5·32 | 3·52 |
| Sulphuric acid | 10·29 | 10·53 | 5·38 | 6·01 |
| Chlorine | 4·93 | 4·68 | 3·23 | 4·56 |
| Carbonic acid | 1·78 | 2·88 | 2·80 | 3·19 |
| Phosphoric acid | 10·66 | 11·27 | 7·06 | 6·65 |
| Silica | 3·81 | 2·61 | 12·75 | 10·52 |
| Sand | 9·32 | 8·08 | 23·10 | 20·19 |
| Total amount | 100·85 | 99·98 | 100·66 | 99·68 |

The first difference which appears upon comparing the two sets of analyses is the absence of soda in coffee, and its presence in chicory to the extent of from 2·04 to 15·1 per cent. of the ash. The united amount of potash and soda does not differ much in the two substances. In chicory, the lime is greater and the magnesia less than in coffee. The sesquioxide of iron is strikingly different, being always under 1 per cent. in coffee, by our experiments, and ranging from 3·13 to 5·32 per cent. in chicory. The ash of chicory is, on this account, red to the eye when compared with that of coffee. The difference in chlorine is also important, the highest proportion observed in coffee-ash being 1·11 per cent., and the lowest proportion in chicory-ash 3·28 per cent. Coffee gives an ash which is highly carbonated, the carbonic acid varying from 14·92 to 18·13 per cent.; while the ash of chicory is only slightly carbonated, containing from 1·78 to 3·19 per cent. of carbonic acid. The proportion of phosphoric acid is pretty similar in the two kinds of ash. The disparity in the silica has been already referred to.

The differences most available in the two kinds of ash, as distinctive tests for coffee and chicory, appear to be the following:—

| | In coffee-ash. | In chicory-ash. |
|---|---|---|
| Silica and sand . | — | 10·69 to 35·85 |
| Carbonic acid . | 14·92 to 18·13 | 1·78 to 3·19 |
| Sesquioxide of iron | 0·44 to 0·98 | 3·13 to 5·32 |
| Chlorine . . | 0·26 to 1·11 | 3·28 to 4·93 |

Another series of ash analyses was executed, comprising the ash of the white lupin of the Levant—a seed which, from its chemical properties and low price, is not unlikely to be substituted for coffee—the ash of acorns, of maize, and of parsnip and dandelion roots.

### Table IX.

Analyses of ashes of certain seeds and roots,

DEDUCTING SILICA, &c.

| | Lupins. | Acorns. | Maize. | Parsnips. | Dandelion root. |
|---|---|---|---|---|---|
| Potash . . . . . . . | 33·83 | 55·49 | 31·28 | 56·86 | 20·22 |
| Soda . . . . . . . | 17·90 | 0·63 | — | — | 34·87 |
| Lime . . . . . . . | 7·81 | 6·98 | 3·11 | 6·88 | 12·87 |
| Magnesia . . . . . . | 6·23 | 4·36 | 14·98 | 6·52 | 1·47 |
| Sesquioxide of iron . . . | — | 0·54 | 0·85 | 0·53 | 1·42 |
| Chlorine . . . . . . | 2·12 | 2·53 | 0·50 | 2·10 | 4·32 |
| Sulphuric acid . . . . . | 6·85 | 4·83 | 4·20 | 4·09 | 2·66 |
| Carbonic acid . . . . . | 0·56 | 13·82 | — | 11·50 | 6·99 |
| Phosphoric acid . . . . | 25·74 | 11·26 | 45·29 | 13·91 | 12·63 |
| Silica, &c. . . . . . . | — | — | — | — | — |
| Total amount . . . . | 101·04 | 100·44 | 100·21 | 102·39 | 97·45 |

Analyses of ashes of certain seeds and roots,

NOT DEDUCTING SILICA, &c.

| | Lupins. | Acorns. | Maize. | Parsnips. | Dandelion root. |
|---|---|---|---|---|---|
| Potash | 33·54 | 54·93 | 30·74 | 56·54 | 17·95 |
| Soda | 17·75 | 0·63 | — | — | 30·95 |
| Lime | 7·75 | 6·01 | 3·06 | 6·85 | 11·43 |
| Magnesia | 6·18 | 4·32 | 14·72 | 6·49 | 1·31 |
| Sesquioxide of iron | — | 0·54 | 0·84 | 0·53 | 1·27 |
| Chlorine | 2·11 | 2·51 | 0·50 | 2·09 | 3 84 |
| Sulphuric acid | 6·80 | 4·79 | 4·13 | 4·07 | 2·37 |
| Carbonic acid | 0·56 | 13·69 | — | 11·44 | 6 21 |
| Phosphoric acid | 25·53 | 11·15 | 44·50 | 13·84 | 11·21 |
| Silica, &c. | 0·87 | 1·01 | 1·78 | 0·57 | 11·26 |
| Total amount | 101·09 | 99·58 | 100·27 | 102·42 | 97·80 |

In the ash only of the dandelion root is the silica sufficiently large in quantity to make a good distinction from coffee. Lupins and maize are distinguished from coffee by their low proportion of carbonic acid. The white lupin, both of the Levant and England, we find to contain a notable quantity of manganese. The oxide of iron is everywhere too low to be serviceable. Chlorine appears as low in maize as in coffee, but the proportion of that element is doubled in lupins, acorns, parsnips,—and nearly quadrupled in dandelion: a high proportion of phosphoric acid distinguishes maize, and we may add all the other cereals, from coffee.

The ash of the turnip root contains, according to Way and Ogston, from 9·54 to 14·82 per cent. of carbonic acid, which is very different from chicory, and nearly as high as in coffee. The sesquioxide of iron of turnip is also given even lower than in coffee, —from 0·14 to 0·66 per cent. Chlorine appears to be as abundant in the turnip, in the form of chloride of sodium, as in the chicory root.

According to the same excellent authorities, in beet-root-ash the carbonic acid varies from 15·23 to 21·61 per cent., and is therefore quite as high as in coffee-ash; the sesquioxide of iron, from 0·52 to 3·74 per cent., small as in coffee; the chlorine very large and distinctive, being represented by from 14·18 to 49·51 per cent. of chloride of sodium.

In the ash of the carrot, the carbonic acid is from 15·15 to 19·11 per cent.; the sesquioxide of iron, from 0·59 to 1·66 per cent.; chlorine nearly as in chicory, being represented by from 4·91 to 7·65 per cent. of chloride of sodium (Way and Ogston).

7. The action of the more ordinary chemical reagents upon infusions of coffee and chicory may now be noted. The indications thus obtained with coffee are unfortunately rendered much less characteristic by the torrefaction of the seed.

TABLE X.

Action of certain chemical reagents upon infusions of coffee and chicory.

| | Raw Coffee. | Roasted Coffee. | Raw Chicory. | Roasted Chicory. |
|---|---|---|---|---|
| Potassa . . | A bright reddish-yellow liquid, and no precipitate. | Brownish-yellow liquid, and no precipitate. | Not altered. | Not altered. |
| Lime-water . . | Pale-yellow liquid ; on standing, becoming green at the surface; no precipitate. | Reddish-brown, with shade of purple, and no precipitate. | Not altered. | Not altered. |
| Acetate of copper | Dirty-green precipitate. | Brownish-green precipitate. | Pale-green precipitate. | Gelatinous precipitate of a reddish-brown colour. |
| Perchloride of iron | Deep greenish-black precipitate. | Very dark greenish-black precipitate. | Blackish-brown-coloured liquid. | No effect. |
| Nitric acid . . | Bright red-coloured liquid. | Clear port-wine-coloured liquid. | No effect. | No effect at first ; on standing, port-wine colour. |
| Sulphuric acid . | Dirty blackish-brown-coloured liquid. | Dark blackish-brown-coloured liquid. | Deep blackish-brown-coloured liquid. | Brownish-black liquid. |
| Hydrochloric acid | Pale brownish-yellow liquid. | Port-wine-coloured liquid. | No effect. | Slightly darkens the liquid. |

In allowing a solution of unroasted coffee to stand, its green colour becomes gradually deeper. This change is due to oxidation and the formation of the viridic acid of Rochleder. It is greatly promoted by the presence of an alkali: an excess of lime brings out this colour very strongly in a day or two,—giving at first, however, a bright yellow colour. Subacetate of lead gives, in unroasted coffee, a yellow precipitate, which does not become green. An excess of acetate of copper gives a green precipitate

in abundance, which is brightened by the addition of an alkali. This copper precipitate has been used as a green pigment. The reactions above described are, however, much altered and obscured by the roasting of the coffee, and are therefore of little service for our present purpose.

It has already been stated that iodine produces no blue coloration in the infusion of either coffee or chicory. If the reagents named act clearly in a different manner upon any infusion from what they do upon pure coffee, a presumption of adulteration is obtained, but the indications must be of a positive and specific nature fully to establish adulteration.

8. Coffee was submitted to the usual process of distillation with soda-lime for the determination of its nitrogen. The proportion of nitrogen per cent. was, in coffee, Sample 1 (Table VII.), roasted, 2·93; in Sample 2, roasted, 2·62; in Sample 3, raw, 2·53, roasted, 2·70; in Sample 4, raw, 2·71; in Sample 5, raw, 2·50, roasted, 2·49. The proportion of nitrogen in roasted coffee appears therefore to lie between 2½ and 3 per cent.

The nitrogen in a specimen of foreign chicory amounted, in the raw chicory, to 1·51 per cent.; in the same roasted, 1·42 per cent. The same of English growth gave, in the raw state, 1·86 per cent. of nitrogen; and in the roasted state, 1·74 per cent.

The proportion of nitrogen in coffee is therefore greater than in chicory; but the difference is not sufficiently marked to distinguish the two substances easily from each other. The conclusion may, however, be drawn, that less than 2 per cent. of nitrogen in coffee is a strong presumption of adulteration.

We may now advert to the peculiar and characteristic substances found in coffee, and the aid to be derived from them in the discovery of adulteration.

9. Professor Rochleder, who has devoted great attention to the analysis of coffee, gives the following enumeration of the substances found in the raw coffee-bean, with the formulæ of their elementary composition:—

| | C. | H. | O. | N. |
|---|---|---|---|---|
| Woody fibre | 12 | 10 | 10 | |
| Cane sugar | 12 | 11 | 11 | |
| Fat: Palmitic acid | 32 | 32 | 4 | |
| Fat: Oleic acid | 36 | 34 | 4 | |
| Fat: Glycerine | 6 | 8 | 6 | |
| Legumin | 48 | 36 | 14 | 6 |
| Caffeic acid | 16 | 7 | 6 | |
| Caffeine | 16 | 10 | 4 | 4 |

To these Rochleder had lately added citric acid ($C_{12}H_5O_{11}$+ 3HO), in the small proportion of 2 grains in a pound of coffee; also a trace, too small to be estimated by weight, of viridic acid ($C_{14}H_6O_7$). This last substance is the acid obtained by exposing solutions of the neutral and basic caffeates to the influence of the air. The green colour of raw coffee is believed by Rochleder to be owing to a small quantity of viridate of lime.

The evidence upon which Rochleder rests the existence of palmitic and citric acids in coffee does not appear to us quite decisive. The formulæ given by that chemist for both caffeic and viridic acids are doubtful.

It is also stated by Rochleder, that when dried caffeic acid is submitted to destructive distillation, a small quantity of crystals were obtained, which he considered to be pyrocatechine. The experiment repeated by us on a considerable scale gave a negative result.

Rochleder finds caffeic acid in Paraguay tea (*Ilex Paraguayensis*), as well as in coffee. This statement we must also doubt. The acid of the Paraguay tea has been examined by us, and found to have a certain resemblance to caffeic acid, but not to be identical with it. Free caffeic acid, when strongly heated in an open vessel, emits the peculiar odour of roasted coffee; but the acid from Paraguay tea emits a perfectly different odour when similarly treated.

The sugar of coffee may be inferred to exist in a peculiar condition, as was before hinted, from the fact that when the coffee is roasted, none of its sugar appears to be converted into grape-sugar, as it does not affect Trommer's test; while, when 7 grains of cane-sugar were added to 100 grains of coffee, and the whole roasted in the usual way, abundant indications of grape-sugar were obtained by the same test.

M. Payen gives the proportional quantities of the different substances which he finds in raw coffee as follows:—

| | |
|---|---|
| Cellular tissue | 34·000 |
| Hygroscopic water | 12·000 |
| Fats | 10· to 13·000 |
| Starch, sugar, dextrin, and vegetable acids | 15·500 |
| Legumin | 1·000 |
| Chlorogenate of potash and caffeine | 3·500 |
| Nitrogenous portion | 3·000 |
| Free caffeine | 0·800 |
| Thick insoluble ethereal oil | 0·001 |
| Aromatic oil | 0·002 |
| Mineral constituents: potash, lime, magnesia, phosphorus, sulphur, silica, and traces of chlorine | 6·697 |

Payen's chlorogenic acid is the same as the caffeic acid of Rochleder and Pfaff. Payen believed that he had obtained from coffee a crystalline double salt of this acid, containing potash and caffeine; but this observation has not been confirmed.

The proportion of fat in the coffee bean is remarkably high, being generally stated at 10 or above 10 per cent. We found at least 8·9 per cent. of fat readily extracted by ether. In chicory the proportion of natural fat is scarcely appreciable; but it is brought up by the fat added in the process of roasting the chicory.

10. Some uncertainty existing respecting the proportion of the active principle, caffeine, in coffee, the point was particularly inquired into. The following process was adopted:—The raw coffee was ground fine, having been previously well dried at 212° to facilitate that operation. A decoction was then made of 1000 grains, by the repeated application of boiling water, so as to exhaust the coffee of all soluble matter. The solution was concentrated a little by evaporation. The acid of the coffee, and certain other substances, were now entirely precipitated by the addition, first, of the neutral acetate of lead, and then of the subacetate of lead. These insoluble matters were removed from the liquid by filtration. The excess of lead in solution was then thrown down by means of hydrosulphuric acid.

The liquid, after this preparation, was evaporated to dryness, and the dry matter left was exhausted by means of strong spirit of wine (sp. gr. 0·840). The alcoholic solution was concentrated by evaporation, and allowed to stand in a nearly syrupy state for about ten days, in order to crystallise. The crystals, which are caffeine, were collected upon a small filter, and compressed powerfully to remove the mother liquor. These crystals were redissolved in a small quantity of water, the solution evaporated, and crystallised anew. It gave almost nothing but caffeine, in long silky white needles, with little or no colour. The proportion of caffeine obtained in five experiments, made upon different samples of coffee, was as follows:—

CAFFEINE IN RAW COFFEE.

| | |
|---|---|
| In Native Ceylon . . . | 0·80 per cent. |
| ,, ,, ,, . . . | 0·80 ,, ,, |
| ,, ,, ,, . . . | 1·01 ,, ,, |
| ,, Plantation Ceylon . . . | 0·54 ,, ,, |
| ,, ,, ,, . . . | 0·83 ,, ,, |

The caffeine of the wild coffee appears to exceed that of the cultivated plant; the mean proportion of caffeine in Native Ceylon being 0·87 per cent., and in Plantation Ceylon 0·69 per cent.

The mean average of the whole five samples is 0·80 per cent. of caffeine. Probably the actual quantity of caffeine in the coffee bean is from 0·75 to 1 per cent., allowance being made for losses in the separation.

The proportion of theine (or caffeine) in tea is considerably greater, and more easily extracted. Two pounds of fine strong Congou yielded 2·93 grains of theine, or 2·09 per cent.

When it is merely desired to extract caffeine from raw or roasted coffee, without reference to quantity, the general process for the extraction of organic bases by means of ether suffices. Lime is added to the infusion of coffee, which is then evaporated to dryness upon a water-bath. The extract may be divided by means of clean sand, and then agitated with ether. The caffeine crystallises as the ether evaporates, or it may be re-dissolved in water, and crystallised again. We believe that the caffeine from 10 per cent. of coffee in a mixture might be extracted in sufficient quantity for its identification by the preceding simple process. Caffeine, when once obtained, is fully recognised by its easy sublimation, and also by its action with nitric acid, in which it resembles uric acid. When the solution of caffeine in nitric acid is evaporated to dryness, and exposed to ammoniacal gas, it is covered by a pink blush, like murexide.

The only other substances besides coffee in which caffeine is known to exist, are tea, Paraguay tea, and a species of chocolate made from the *Gaurana officinalis* or *Paullinia sorbilis.*

11. Chemists generally are disposed to refer the flavour and peculiar properties of coffee, as a beverage, more to its acid—the *caffeic acid* (particularly after that substance is modified in its properties by roasting), than to any other constituent of the seed. Rochleder considers this acid as belonging to the tannin class of substances, and calls it tanno-caffeic acid. But as caffeic acid does not precipitate gelatine, it is deficient in the most characteristic quality of the tannic acids. Caffeic acid, in the present state of our knowledge, appears to be confined to the coffee plant.

We have observed a property of caffeic acid which facilitates the detection of that substance, and consequently of coffee, in a mixture. Caffeic acid appears to be analogous to kinic acid, the acid of cinchona barks, for it yields kinone when oxidated by means of sulphuric acid and binoxide of manganese. To observe this property, the coffee is boiled with water and a little slaked lime, the infusion filtered, and evaporated down to the consistence of a syrup. The syrupy liquid is then mixed in a retort with four times its weight of binoxide of manganese, and 1 part of oil of vitriol diluted with an equal bulk of water. Sufficient heat is

produced by the action of sulphuric acid upon the other materials, to bring over the greater portion of the kinone, and the lamp need not be applied till towards the close of the operation. The distillate consists of yellow crystals of kinone, which usually coat the neck and sides of the retort, and a bright yellow liquid, which is a saturated aqueous solution of kinone, with a considerable quantity of formic acid. Kinone is easily discernible by its volatility and peculiarly acrid odour, which greatly resembles that of chlorine. The solution of kinone gives with ammonia a sepia-black colour, and becomes reddish brown with hydrosulphuric acid. It is decolorised by sulphurous acid. The beautiful green hydrokinone is obtained by exactly neutralising the solution of the yellow kinone with sulphurous acid, great care being taken not to introduce the latter in excess.

The peculiar acid of Paraguay tea agrees with caffeic acid (to which it is no doubt related) in yielding kinone to similar oxidising agencies: so does the acid of the leaves of common holly (*Ilex aquifolium*), tea, and the whole of the *cinchona* tribe.

The *prune* tribe of plants, including the sloe, cherry, laurel, &c., the seeds of which yield prussic acid, all contain amygdalin, or some similar principle. Now all of these, when oxidised in the same manner as the former class, yield oil of bitter almonds, and so can be recognised.

The *willow* and *poplar* tribe, on the other hand, yield oil of *Spirea ulmaria* (salicylous acid), a very characteristic substance.

The tests for kinone can be applied in a few minutes, and they are sufficient to indicate the presence of 10 or 12 per cent. of coffee in a mixture.

12. The root of *chicory* presents no feature of a marked nature, beyond its large proportion of sugar and the composition of its ash, which have both been sufficiently adverted to. The proportion of fat naturally in the root is quite insignificant. In an infusion of the fresh undried root, neutral acetate of lead appears to throw down the whole acids of chicory, and the subacetate of lead produces no further precipitate in the liquid. But the root appears to undergo a considerable modification by being dried at a temperature not exceeding 212°. Its infusion now gives a second precipitate with subacetate of lead following the neutral acetate. Both of these precipitates can be well enough washed; but when the attempt was made to decompose either of them by means of hydrosulphuric acid, a mucilaginous liquid was obtained, from which the sulphide of lead does not fall, unless with a considerable addition of alcohol. The acid precipitates appear most indeterminate, and afford nothing crystalline. A great deal of pectin-looking substance is present. Chicory also appears to

possess about one-fourth of the quantity of inulin that is contained in the dahlia root, and starch in no other form, the infusion of chicory giving only a brown with iodine, and no blue. Chicory appears to contain no oxalic, malic, citric, or any other crystallisable organic acid. The other sweet roots, beet, turnip, &c., also, like chicory, present little that is tangible in their chemical properties. But the high colour of the infusions of all these roots when roasted, the great density of their solutions, and their fermentability, afford sufficient means for distinguishing them from coffee, and for discovering their admixture with that substance.

The properties of a great variety of other vegetable substances, which might possibly be employed in the adulteration of coffee, are exhibited in the early tables of this Report.

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